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Innovative Thermal Processes for Hazardous Waste Treatment and Destruction

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INNOVATIVE THERMAL PROCESSES FOR HAZARDOUS WASTE TREATMENT AND DESTRUCTION

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As the land disposal of untreated hazardous wastes has continued to fall into disfavor in North America, increasing attention is being given to alternative hazardous waste treatment and disposal technologies. This increased attention and the public and private support resulting from such attention have resulted in the development over the past several years of many very innovative processes. This paper, which is based upon the survey of innovative thermal processes carried out by the staff of the U.S. Environmental Protection Agency's Hazardous Waste Engineering Research Laboratory in Cincinnati, Ohio, discusses six innovative processes currently being discussed in governmental, academic, and industrial circles in the United States and Canada.

- High Temperature Electric Reactor
- Wet Oxidation Process
- Plasma Arc Technology
- Supercritical Water
- Molten Glass Incineration
- Molten Salt Reactor

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INNOVATIVE THERMAL PROCESSES FOR HAZARDOUS WASTE TREATMENT AND DESTRUCTION

ABSTRACT

As the land disposal of untreated hazardous wastes has continued to fall into disfavor in North America, increasing attention is being given to alternative hazardous waste treatment and disposal technologies. This increased attention and the public and private support resulting from such attention have resulted in the development over the past several years of many very innovative processes. This paper, which is based upon a survey of innovative thermal processes carried out by the staff of the U.S. Environmental Protection Agency's Hazardous Waste Engineering Research Laboratory in Cincinnati, Ohio, discusses six innovative processes currently being discussed in governmental, academic, and industrial circles in the United States and Canada.

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- Wet Oxidation Process
- Plasma Arc Technology
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Introduction

There are today in various stages of development in the United States and Canada many new thermal processes for treating and destroying all types of hazardous wastes. While some of these processes are essentially improvements on conventional treatment and destruction methods, other processes represent entirely new and innovative approaches to waste treatment and destruction. This paper discusses six such innovative thermal processes:

- High Temperature Electric Reactor
- Wet Oxidation Process
- Plasma Arc
- Supercritical Water Process
- Molten Glass Incineration
- Molten Salt Reactor

A summary of these processes is shown in Table 1.

TABLE 1. PROCESS SUMMARY

Process Name	Description	Waste Streams	State of Development	Test Data Available	Cost Data Available	For Information Contact
Huber Advanced Electric Reactor	Uses electrical heat to pyrolyze organic materials at extremely high temperatures	Finely ground solids	C	A	1	J. M. Huber Corporation P. O. Box 2831 Borger, TX 79007 (806) 274-6331
Zimpro Wet Air Oxidation	Uses elevated temperature and pressure to oxidize organics in water	Aqueous streams with less than 5% organics	C	A	1	William Copa Zimpro, Inc. Military Road Rothschild, WI 54474 (715) 359-7211
Pyrolysis Systems Pyroplasma	Uses plasma arc device to create extremely high temperatures for waste destruction	Highly toxic liquids	P	C	2	Pyrolysis Systems, Inc 4935 Kent Street Niagara Falls, Ontario L2H 1J6 Contact: Mr. Ian Thom
MODAR Supercritical Fluid Oxidation	Uses high temperatures and very high pressure to oxidize organic contaminants in water	Aqueous slurries or organic solutions	P	D	3	MODAR, Inc. 14 Tech Circle Natick, MA 01760 (617) 655-7741
Penberthy Electromelt Pyro Converter	Uses a bed of molten glass to oxidize organics and to capture ash and inorganics	Any liquid or solid waste stream	C*	NA	2	Penberthy Electromelt International, Inc. 631 South 96th Street Seattle, WA 98108 (206) 762-4344
Rockwell International Molten Salt Destruction	Uses a bed of molten sodium carbonate to destroy wastes and scrub acid gases	Low ash, low water content, solid or liquid wastes	P	A	NA	Rockwell International Environmental and Energy Systems Division 8900 De Soto Avenue Canoga Park, CA 91304 (213) 700-8200

Legend for Table 1

State of Development
- C - Commercially available
- C* - Commercially available for other than hazardous wastes
- P - Pilot scale
- B - Lab and bench scale
- Co - Conceptual

Test Data Available
- A - Sponsored by EPA or other third party
- B - Company sponsored tests
- C - Company sponsored pilot scale tests
- D - Company sponsored bench scale tests
- NA - Not Available

Cost Data Available
- 1 - Based on commercial scale operation
- 2 - Estimates based on pilot scale operation
- 3 - Estimates based on bench scale operation
- NA - Not Available

HIGH TEMPERATURE ELECTRIC REACTOR

Process Description

The high temperature electric reactor employs a new technology to rapidly heat materials to temperatures in the range of 2200°C using intense thermal radiation in the near-infrared region. The reactants, which can be in gaseous, liquid, or solid form, are isolated from the reactor core walls by means of a gaseous blanket formed by flowing nitrogen radially inward through the porous core walls. Carbon electrodes implanted in the wall of the reactor are heated and in turn heat the reactor core to incandescence so that heat transfer is accomplished by thermal radiative coupling from the core to the feed materials. The only feed streams to the reactor are the solid, liquid, or gaseous wastes and the blanket gas, nitrogen. Destruction is accomplished by pyrolysis rather than oxidation. Therefore, typical products produced by incineration, such as carbon monoxide, carbon dioxide, and oxides of nitrogen, are not formed in significant concentrations. The principal products of soil-borne PCB destruction using this process are H_2, Cl_2, HCl, elemental carbon, and a granular, free-flowing, solid-derived material. Figure 1 is a simplified process diagram of the HTG process. For solid waste treatment, the solid feed stream is introduced at the top of the reactor by means of a metered screw feeder connecting the air-tight feed hopper to the reactor. Nitrogen is introduced primarily at two points in the reactor annulus formed by the external containing vessel and the porous graphite core which creates the fluid wall. The solid feed passes through the reactor where pyrolysis occurs at temperatures above 2200°C (4000°F). After leaving the reactor, the product gas and waste solids pass through two post-reactor treatment zones (PRTZ). The PRTZ is an insulated vessel to provide additional high temperature (in excess of 1100°C, 2000°F) and residence time (5 to 10 seconds) while the second PRTZ is water-cooled. It also provides additional residence time (approximately 10 seconds) but primarily cools the gas to less than 540°C (1000°F) prior to downstream particulate cleanup.

Solids exiting the PRTZ are collected in a solids bin which is sealed to the atmosphere. Additional solids in the product gas are removed by a cyclone and routed back to the solids bin. The product gas then enters a baghouse for fine particle removal followed by an aqueous caustic scrubber for chlorine removal. Any residual organics and chlorine are removed by passing the product gas through activated carbon beds just upstream of the emission stack. The organic, particulate, and chlorine-free product gas composed almost entirely of nitrogen is then emitted to the atmosphere through the process stack.

Suitable Wastes

The process is primarily designed to pyrolize organics attached to particulates such as carbon black or soil. However, recent tests have shown that the process is also effective for liquid refractory waste streams such as carbon tetrachloride.

State of Development

Huber maintains two fully equipped Advanced Electric Reactors in Borger, Texas. The smaller reactor, which as a nominal core diameter of 3 inches, is used for proof-of-concept experiments. The largest reactor, which is of commercial scale, has a 30cm (12-inch) core diameter but is used primarily for research purposes.

It is anticipated that by the second quarter of 1985 Huber will have a transportable commercial scale unit ready for the demonstration of treating dioxin-contaminated soil. A 50,000 ton per year unit can be available in early 1986 if applications are identified.

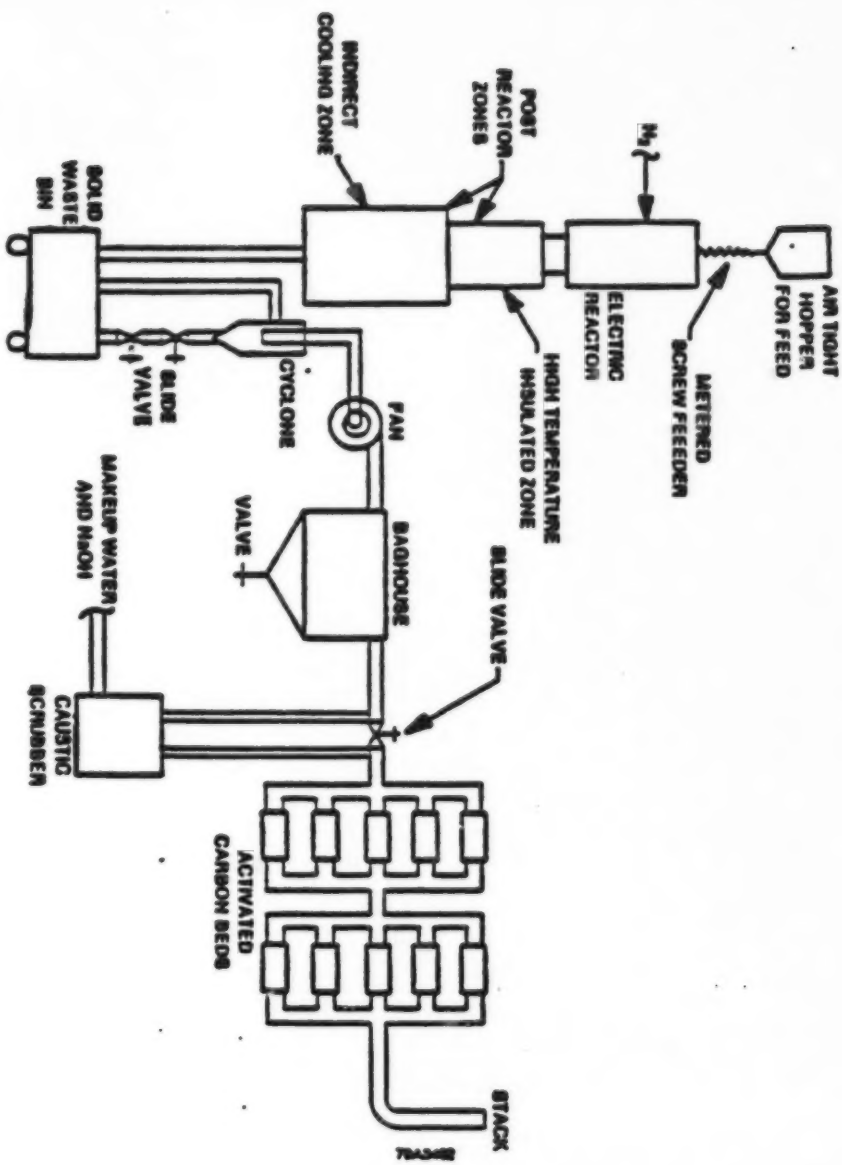

Figure 1 Electric Reactor

WET AIR OXIDATION

Process Description

Wet air oxidation refers to the aqueous phase oxidation of dissolved or suspended organic substances at elevated temperatures and pressures. Water, which makes up the bulk of the aqueous phase, serves to modify oxidation reactions so that they proceed at relatively low temperature (170°C to 350°C) and at the same time serves to moderate the oxidation rates removing excess heat by evaporation. Water also provides an excellent heat transfer medium which enables the wet oxidation process to be thermally self-sustaining with relatively low organic feed concentrations.

An oxygen-containing gas, usually air, is bubbled through the liquid phase in a reactor used to contain the process, thus the commonly used term "wet air oxidation" (WAO). The process pressure is maintained at a level high enough to prevent excessive evaporation of the liquid phase.

The basic flow scheme of a continuous WAO system is shown in Figure 2. A wastewater stream containing oxidizable contaminants is pumped to the system pressure by means of a positive displacement-type pump. The wastewater passes through a heat exchanger which preheats the waste by indirect heat exchange with the hot oxidized effluent. The temperature of the incoming feed is increased to a level necessary to support the oxidation reaction in the reactor vessel. Air and the incoming liquid are injected into the reactor where the oxidation begins to take place. As oxidation progresses up through the reactor, the heat of combustion is liberated, increasing the temperature of the reaction mixture. This heat of oxidation is recovered by interchanging with the incoming feed thus giving thermally self-sustaining operation. After energy removal, the oxidized effluent, comprised mainly of water, carbon dioxide, and nitrogen is reduced in pressure through a specially designed automatic control valve.

Of all variables affecting wet air oxidation, temperature has the greatest effect on reaction rates. In most cases, about 125°C is the lower limit for appreciable reaction, about 240°C is needed for reaction to the 80 percent reduction of Chemical Oxygen Demand (COD) range, and at least 300°C is needed for 95 percent reduction of COD or better reaction within practical reaction time.

Initial reaction rates and rates over the first 30 minutes are relatively fast. After about 60 minutes, rates become so slow that generally little increase in percent oxidation is gained in extended reaction.

WAO can reduce toxicant/contaminants to compounds such as H_2O, CO_2, and various simple acids depending upon the waste in question. Specific toxic compounds such as the priority pollutants, phenols, cyanides, DDT, nitrosamines, and many carcinogens can be reduced by WAO. The effluent liquor is suitable for either final discharge or is readily degradable if further biological treatment is desired.

The products of WAO stay in the liquid phase and do not create a secondary air pollution problem. Off-gases from a WAO system are free of NO_x, SO_2, and particulate. Water scrubbing is usually used to eliminate any odors.

Suitable Waste Streams

The process is designed for wastes too dilute to incinerate economically, yet too toxic to treat biologically.

WAO also has application for inorganic compounds combined with organics. The oxidation cleans up the mixture for further removal of the inorganics. WAO can detoxify most of the EPA priority pollutants. A destruction of 99.8 percent of the initial priority pollutant can be achieved by WAO between 527°F and 608°F. Toxic removal parameters are in the order of 99+ percent using short-term, acute, static toxicity measurements.

State of Development

This process is available at commercial scale. The USEPA and the State of California are supporting the demonstration of a 40 l/min unit at Casmalia Resources near Santa Maria, California.

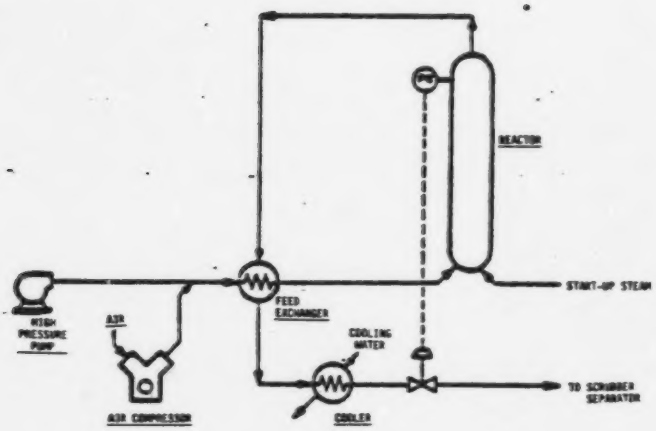

Figure 3: Basic Flowsheet of the Wet Air Oxidation Process

PLASMA ARC

Process Description

A plasma is a gas consisting of charged and neutral particles with an overall charge near zero. A plasma arc is generated by electricity and can reach temperatures up to 27,000°C. When applied to waste disposal, the plasma arc can be considered as an energy conversion and energy transfer device. The electrical energy is transformed into a plasma. As the activated components of the plasma decay, their energy is transferred to the waste materials exposed to the plasma. The wastes are ultimately decayed and destroyed as they interact with the decaying plasma.

The plasma arc device that forms the heart of this process is fabricated from stainless steel and is refractory lined to limit heat loss. A co-linear electrode arrangement creates an electric arc which is stabilized by field coil medium through which an electric current is passed. In passing through the air, the electrical energy is converted to thermal energy by adsorption by the air molecules which are activated into ionized atomic states, losing electrons in the process. Ultraviolet radiation is emitted when the molecules or atoms relax from their highly activated states to lower energy levels. Waste fluids are injected into the plasma zone to interact with decaying plasma species to become rapidly atomized prior to exiting this electrode space.

In a mobile prototype of this process, a five hundred kilowatt plasma device is fitted to one end of a stainless steel reaction chamber and mated to a hollow graphite core to form an atomization zone. Residence time in this atomization zone is approximately five hundred micro-seconds. The reaction chamber serves as the equilibration zone where the atomized species recombine to form new products. This zone is equilibrated at a temperature range of 1200-1800 Kelvin and the residence time in this zone is approximately one second. All hardware is designed to be located within a forty-five foot long moving van-type trailer.

During normal operation, the plasma pyrolysis unit requires approximately three minutes of warmup time prior to commencing injection of toxic or hazardous wastes. During warmup, the system is injected with a flushing fluid such as ethanol to maintain a reducing atmosphere inside the atomization zone. This unit also requires approximately twenty minutes to cool key components in order to conduct post run maintenance. These short cycle times make this unit basically an on/off system which can respond rapidly to adverse conditions. The system hardware is arranged to provide failsafe operation even in the event of total power failure.

Suitable Waste Streams

The plasma arc is designed for highly toxic liquid waste streams such as leachates from remedial clean-up operation.

State of Development

The testing of this technology has been the subject of continuing support from the EPA and the New York State Department of Environmental Conservation. The fabrication of a mobile unit capable of treating from one to two and a half gallons per minute of waste was completed in the Spring of 1984. A four stage demonstration of the mobile unit is currently underway in Kingston, Ontario, Canada.

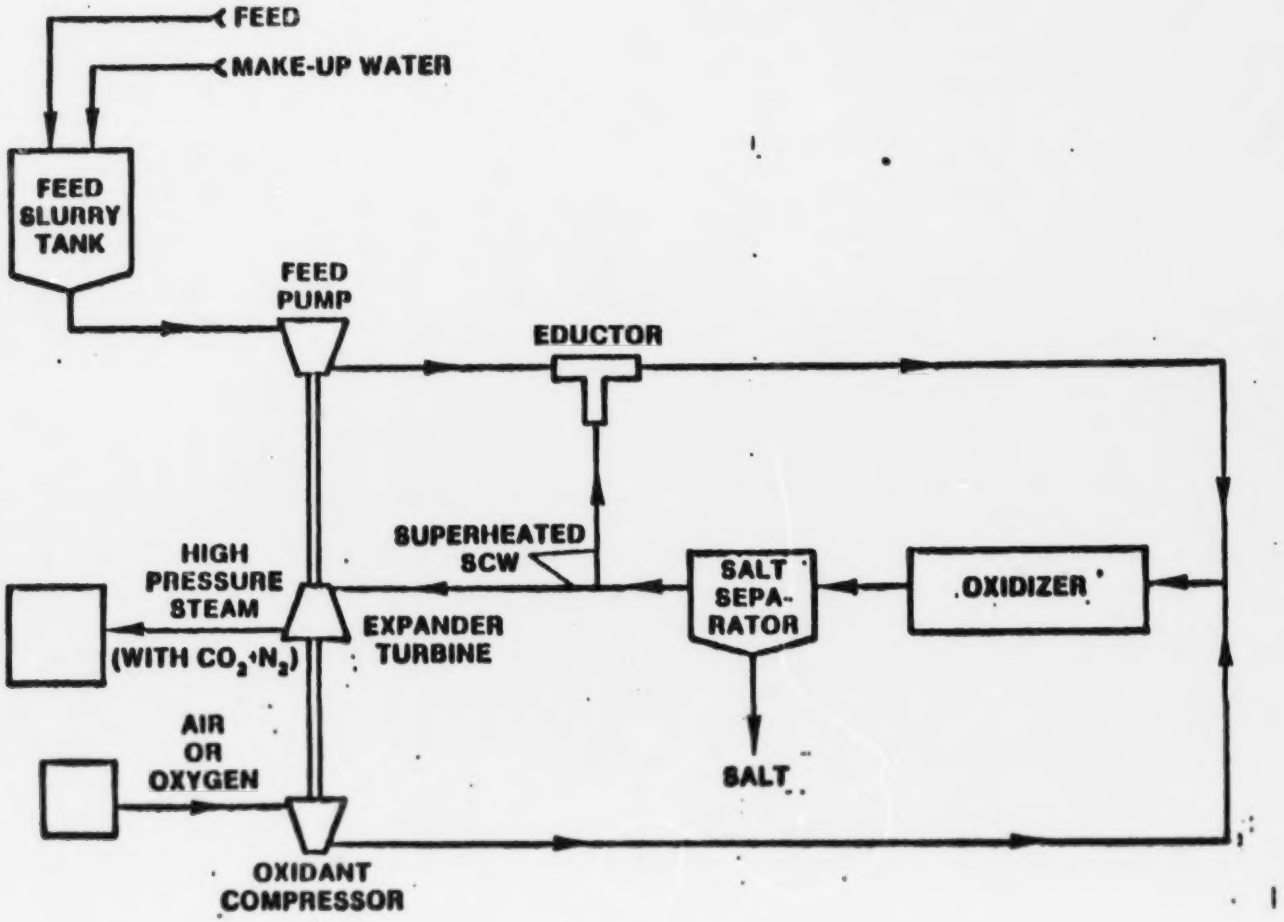

Figure 3 Schematic Diagram of the Modar Supercritical Water Process

SUPERCRITICAL WATER

Process Description

In the supercritical water process an aqueous waste stream is subjected to temperatures and pressures above the critical point of water, i.e. that point at which the densities of the liquid and vapor phase are identical. (For water the critical point is 379°C and 218 atmospheres). In this supercritical region water exhibits unusual properties that enchance its capability as a waste destruction medium. Because oxygen is completely miscible with supercritical water, the oxidation rate for organics is greatly enhanced. Also inorganics are practically insoluble in supercritical water. This factor allows the inorganics to be easily removed from the waste streams. The total result is that organics are oxidized extremely rapidly and the resultant stream is virtually free of inorganics.

A patented process has been developed by MODAR that incorporates the properties of supercritical fluids to oxidize organic contaminants in aqueous streams.

A schematic of the process is shown in Figure 7. A brief summary of the process is:

a. Waste is slurried with make-up water to provide a mixture of 5 percent organics. The mixture is heated using previously processed supercritical water and then pressurized.

b. Air or oxygen is pressurized and mixed with the feed. Organics are oxidized in a rapid reaction. (Reaction time is less than 1 minute.) For a feed rate of 5 wt. percent organics, the heat of combustion is sufficient to raise the oxidizer effluent to 500°C.

c. The effluent from the oxidizer is fed to a salt separator where inorganics are precipitated out.

d. Waste heat from the process can be reclaimed to provide sufficient energy for power generation and high pressure steam.

Suitable Waste Streams

The MODAR SCW process is designed for aqueous waste streams containing high levels of inorganics and toxic organics.

State of Development

The process has been under development since 1980 and is currently being demonstrated in a unit with a capacity of from 400 to 8000 liters per day of aqueous wastes.

MOLTEN GLASS INCINERATION

Process Description

The integral part of this process is an electric furnace approximately 22' long and 3' wide that has a pool of molten glass covering the bottom. This type of furnace is used extensively in the glass manufacturing industry to produce glass. When used as a waste incinerator the unit utilizes the extremely high temperatures in the combustion chamber to destroy organic waste streams.

Waste materials, both combustible and non-combustible, are charged directly into the combustion chamber above the pool of molten glass. The waste can either be contained in fiberboard boxes, or uncontained in loose form. The temperatures of the pool of molten glass are maintained above 2300°F (1260°C) by use of electrodes immersed in the pool. Combustible wastes are oxidized above the pool, and inorganics and ash fall onto the pool where they are melted into the glass.

Liquid and slurry wastes are introduced at a controlled rate through a pipe. If the liquid base is water, the water boils to steam, progressively leaving solids behind. If the liquid is oil, toluene or other organics, the liquid burns to CO_2, H_2O and HCl (if a chlorinated compound). Dirt and non-combustible content drop onto the glass and melt in. The gases go up through the filter to the spray chambers where the HCl is converted to common salt (NaCl). Wet spent ion-exchange resins first lose water and then burn as above. Complementary raw materials if needed are charged into the furnace via a screw charger.

The flue gases pass through a set of ceramic fiber filters. When each filter in turn is loaded with pollutants, it is pushed into the furnace where it dissolves, capturing the dust into the glass. The flue gases then go through a gas-to-water heat exchanger and then to two water spray chambers. The water in the second chamber is fairly pure to prevent loaded water from passing onward into the rest of the system. The demist chamber takes out practically all of the droplets. The gases are then reheated above the dew point. The gases then pass through charcoal and HEPA filters before going to the blower and out the vent stack.

Filter sludge from the spray chambers, the charcoal, and HEPA filters are disposed of in the furnace. The charcoal burns to carbon dioxide and the dust and sludges are melted into the glass. HEPA filters (not metal parts) melt into the glass pool, capturing their contained dust.

The glass is tapped off into canisters from time to time as necessary. After cooling, the canisters are ready for final disposal.

The entire system is maintained under negative pressure by means of the exhaust blower. Combustion air is admitted to the furnace through ports which control oxygen as desired, usually 4% minimum for completeness of combustion.

Suitable Waste Streams

The system is designed to accept liquid and solid wastes, including wastes with high ash and inorganics content.

State of Development

The process is being offered commercially. Potential waste disposal capacities of units range from 20 kg/hour to 4,000 kg/hour.

MOLTEN SALT DESTRUCTION

Process Description

Molten salt destruction is a method of combusting organic material while, at the same time, scrubbing in-situ, objectionable by-products of that combustion and thus preventing their emission in the effluent gas stream. This process of simultaneous combustion and scrubbing (Figure 4) is accomplished by injecting the material to be burned with air, or oxygen enriched air, under the surface of a pool of molten sodium carbonate. The melt is maintained at temperatures on the order of 900°C causing the hydrocarbons of the organic matter to be immediately oxidized to carbon dioxide and water. The combustion by-products containing such elements as phosphorus, sulfur, arsenic, and the halogens react with the sodium carbonate. These by-products are retained in the melt as inorganic salts rather than released to the atmosphere as volatile gases. In time, inorganic products resulting from the reaction of organic halogens, phosphorus, sulfur,etc., build up and must be removed from the molten bed to retain its ability to absorb acidic gases. Ash introduced by the waste must be removed to preserve the fluidity of the melt. An ash concentration in the melt of about 20 percent by weight provides an ample margin of safety to maintain melt fluidity. Melt removal can be done continuously or batchwise.

The Rockwell International molten salt combustor is a proprietary design. The system was originally developed as a gasifier for coal. For waste combustion, the unit is operated at a temperature of from 800°C to 1000°C, a temperature high enough to completely destroy most hazardous wastes and keep the salt molten, and low enough to avoid NO_x emissions.

Depending upon the size and design application of the particular unit, the salt in the bed is recovered or disposed of when it becomes excessively laden with ash or products of acid gas reaction. The process can operate at atmospheric pressure or elevated pressure.

Since beginning the development of molten salt combustion technology in 1969, Rockwell has constructed several units of varying sizes. The company is currently operating three sizes of units; bench scale combustors for feeds of up to 5 kg/hr of wastes, a pilot scale unit for feeds of up to 125 kg/hr of wastes, and a production-scale unit which operated successfully as a coal gasifier for up to 1000 kg/hr of coal. Commercial systems are now being offered for specific wastes. A prototype portable system of 100 kg/hr is under construction.

The combustor was originally constructed as a refactory-lined steel vessel. Recent developments have shown that some specific engineering alloys are suitable for containment of the molten salt bed. The metal combustor provides for improved reliability, lower cost and increased waste throughout by using external heat transfer.

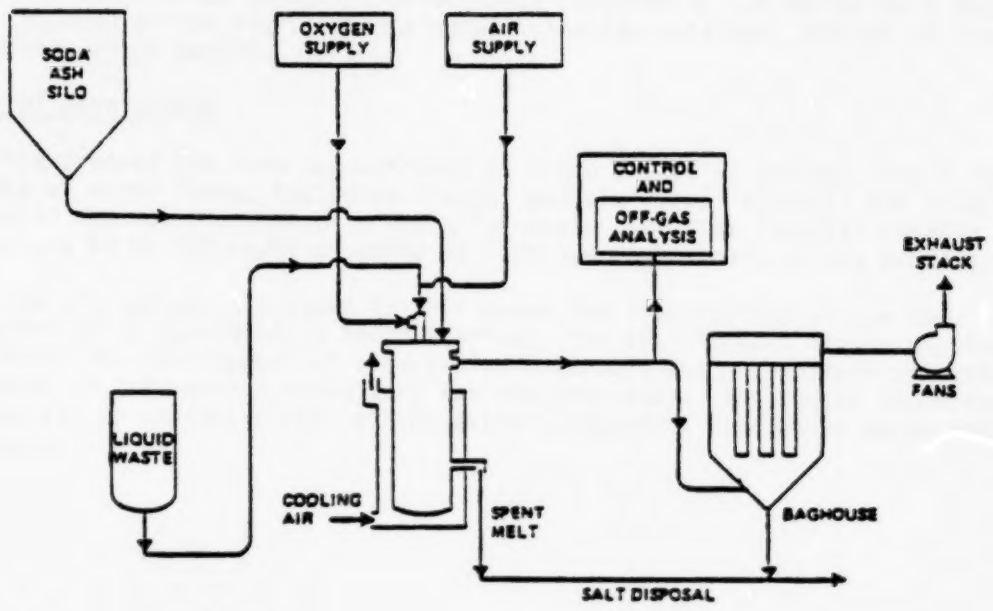

Figure 4 Simplified Diagram of the Molten Salt Waste Destruction Process.

Suitable Waste Streams

Molten salt destruction is designed for liquids, granulated or shredded solids, and slurries with ash contents of less than 20 percent. The process is especially applicable for wastes whose combustion results in acids being liberated since these acids are effectively captured by the molten salt $NaCO_3$ bed. Because of the high destruction efficiencies obtained, MSD can be used for highly toxic wastes.

State of Development

The process has been demonstrated at bench and pilot scales, with a large variety of waste forms, including fluids, and slurries. Rockwell has recently completed the construction of a new pilot scale combustor facility capable of combusting 40 to 100 kg/hr of waste to continue development of the process.

The six systems discussed in this paper are illustrative of the new processes being developed in North America. The EPA, as part of its mission to further the development of alternative hazardous waste treatment processes, maintains an information repository for new processes. Interested individuals are invited to contact either of the authors regarding innovative waste treatment processes.

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